The origin of dark inclusions in Allende: New evidence from lithium isotopes

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Abstract–Aqueous and thermal processing of primordial material occurred prior to and during planet formation in the early solar system. A record of how solid materials were altered at this time is present in the carbonaceous chondrites, which are naturally delivered fragments of primitive asteroids. It has been proposed that some materials, such as the clasts termed "dark inclusions" found in type III chondrites, suggest a sequence of aqueous and thermal events. Lithium isotopes (^{6}Li and ^{7}Li) can reveal the role of liquid water in dark inclusion history. During aqueous alteration, ^{7}Li passes preferentially into solution leaving ^{6}Li behind in the solid phase and, consequently, any relatively extended periods of interaction with ^{7}Li-rich fluids would have left the dark inclusions enriched in the heavier isotope when compared to the meteorite as a whole. Our analyses of lithium isotopes in Allende and its dark inclusions reveal marked isotopic homogeneity and no evidence of greater levels of aqueous alteration in dark inclusion history.

INTRODUCTION

Asteroids comprise materials that eventually formed larger planet-sized bodies in the early solar system. The study of asteroids enables us to understand the aqueous and thermal history of planetesimals prior to and during planet formation. A class of meteorite termed the "carbonaceous chondrites" are fragments of primitive asteroids and contain materials such as carbonates and phyllosilicates that are generally considered to be evidence of liquid water on the meteorite parent body. Yet the role of water and heat in the generation of other components is less well understood.

For instance, CV3 chondrites contain numerous dark and angular clasts that range in size from a few millimeters to a few centimeters (Fruland et al. 1978; Johnson et al. 1990). These so-called "dark inclusions" are complex brecciated structures containing clasts, aggregates, chondrules, mineral fragments, and dark, fine-grained matrices. Recent data from CO3 chondrites indicate that dark inclusions also occur in other type III chondrites, although these inclusions are mostly smaller in size (Itoh and Tomeoka 2003).

Chemical and petrological data suggest that dark inclusions are genetically related to the host meteorite and not clasts from another parent body (Fruland et al. 1978). Dark inclusions are considered to be either primary aggregates of condensates from the solar nebula (e.g., Kurat et al. 1989) or areas that have undergone aqueous alteration and subsequent dehydration (e.g., Kojima et al. 1993). The provenance of dark inclusions remains contentious, and constraining the origin of such materials is essential to understanding the aqueous and thermal history of contributing materials during the formation of planets.

One technique that reveals the role of liquid water in producing components on meteorite parent bodies is lithium isotopes (^{7}Li, ^{6}Li). Studies of continental weathering processes suggest that, during low-temperature (<~300 °C), mineral-fluid interactions, ^{6}Li is preferentially retained in the solid phase, while ^{7}Li passes into solution (Huh et al. 2001; Kisakürek et al. 2004, 2005). The reason for ^{7}Li-enrichment in the fluid is discussed in Huh et al. (2001). As might be expected, during weathering, bonds containing ^{6}Li break preferentially and during diffusion, ^{6}Li travels faster than ^{7}Li (e.g., Richter et al. 2006). However, when it comes to fluid-rock interactions, it is the high vibrational frequency of water (1600–3900 cm^{-1}) compared to common minerals (<1000 cm^{-1}) that dominates lithium isotope fractionation and water has a tendency to incorporate ^{7}Li preferentially. This hydration effect is very strong for lithium and overrides

the effects of bond breaking and diffusion, so the fluid phase becomes enriched in the heavy isotope. This concept has been supported by a recent study of inorganic phases in the Murchison meteorite that revealed dramatically increased ^7Li contents in the aqueously generated phyllosilicate-rich matrix and carbonate phases (Sephton et al. 2004).

Investigations of the lithium isotope composition of a number of whole rock chondrites disclose that variations are the consequences of different relative abundances of ^7Li-rich phyllosilicates (McDonough et al. 2003) and carbonates (Sephton et al. 2004) relative to ^7Li-poor, non-aqueously generated phases. The data imply that increased ^7Li concentrations are indicators of past aqueous activity. Moreover, it has been suggested that subsequent dehydration of aqueous altered materials does not remove ^7Li enrichments (McDonough et al. 2003); there is a variety of evidence to support this inference. Experimental and field data that indicate that lithium isotopes are not fractionated during phase separation (Foustoukos et al. 2004) and a study of extraterrestrial materials failed to find any evidence for lithium isotope fractionation related to the depletion of volatiles (Magna et al. 2006). Thus, complex thermal histories are unlikely to preclude the identification of past aqueous events. In this paper we report lithium isotopic analyses that provide insight as to the past aqueous history of the Allende dark inclusions.

EXPERIMENTAL

In addition to a whole rock sample, individual dark inclusions were hand-picked from a sample of Allende (Table 1). Prior to isotopic analysis, samples were ground to a fine powder in an agate pestle and mortar. For bulk analysis (i.e., the analysis of individual pieces of whole rock Allende or its dark inclusions without sequential leaching steps), between 10 and 50 mg of each sample was weighed into a screw-capped Teflon vial and dissolved in 1 ml of 15 N thermally-distilled (TD) HNO_3 and 4 ml TD HF on a hotplate (130 °C, 24 hr). The solution was evaporated to incipient dryness, 2 ml of 15 N TD HNO_3 added and then refluxed (130 °C, 24 hr). Following a final evaporation step, the residue was taken up in 100 μl of 0.2 N TD HCl for lithium isotopic analysis.

A separate ~40 mg aliquot of each sample was also subject to a sequential leaching procedure. Firstly, to isolate easily soluble salts, the sample was ultrasonicated with 1 ml of TD H_2O for 30 min. The leachate was then separated from the residue by centrifugation, the procedure repeated, and the wash solutions combined. Secondly, 2 ml of 1N TD acetic acid were added to the residue in order to isolate any carbonate material (and other acetic-acid soluble phases, which are likely to include Fe-oxides and Fe-oxyhydroxides). This mixture was heated on a hotplate at 50 °C for 24 hr. The leachate was separated from the residue by centrifugation; the

Table 1. Lithium concentration and lithium isotope analyses of Allende: whole rock and dark inclusions.

Sample	[Li][a]	$^7Li/^6Li$[b]	δ^7Li (‰)
Whole rock Allende			
Bulk	1.5 ppm	12.0440	+2.0
Acetic acid leach	0.10 ppm	12.0633	+3.6
Bulk minus acetic leach	(1.4 ppm)	12.0512	+2.6
Dark inclusion 1a1-1			
Bulk	1.2 ppm	12.0416	+1.8
Bulk		12.0452	+2.1
Dark inclusion 1a1-2			
Bulk minus leaches	1.0 ppm	12.0464	+2.2
Water leach	5.7 ppb	12.3325	+26
Acetic acid leach	0.26 ppm	12.0476	+2.3
Dark inclusion 2a2			
Bulk	1.6 ppm	12.0512	+2.6
Bulk minus leaches	(1.3 ppm)	12.0464	+2.2
Water leach	3.3 ppb	12.2364	+18
Acetic acid leach	0.27 ppm	12.0512	+2.6
Dark inclusion 5a1			
Bulk	1.1 ppm	12.0488	+2.4
Bulk		12.0464	+2.2
Bulk minus leaches	(0.9 ppm)	12.0416	+1.8
Water leach	1.5 ppb	12.2123	+16
Acetic acid leach	0.18 ppm	12.0512	+2.6
Dark inclusion 12b1			
Bulk	1.7 ppm	12.0428	+1.9
Bulk minus leaches	(1.5 ppm)	12.0404	+1.7
Water leach	6.2 ppb	12.2123	+16
Acetic acid leach	0.17 ppm	12.0573	+3.1
Dark inclusion 14b1			
Bulk	1.4 ppm	12.0512	+2.6
Bulk minus leaches	(1.2 ppm)	12.0452	+2.1
Water leach	2.2 ppb	12.2003	+15
Acetic acid leach	0.25 ppm	12.0404	+1.7
Dark inclusion 3876			
Bulk	1.3 ppm	12.0416	+1.8
Bulk minus leaches	(1.0 ppm)	12.0404	+1.7
Water leach	0.8 ppb	12.3205	+25
Acetic acid leach	0.30 ppm	12.0344	+1.2

[a] Concentrations estimated from MC-ICP-MS signal intensity; precision is approximately ±10%. Brackets indicate values obtained by subtraction; all other values were measured directly.

[b] $^7Li/^6Li$ ratios are calculated using the equation and the absolute $^7Li/^6Li$ value for the L-SVEC standard (12.02).

residue was then washed in TD H_2O (×3) and the wash solutions were added to the leachate. Finally, the residue was treated with HNO_3/HF as described above for the bulk analysis in order to isolate acetic-acid insoluble phases, which are mainly silicates and other refractory minerals. All leachates were evaporated to incipient dryness and taken up in 100 μl 0.2N TD HCl for lithium isotope analysis.

Solutions for lithium isotope analysis were first passed through a cation exchange column to separate lithium

Table 2. Lithium isotope ratios of terrestrial and extraterrestrial sources and materials.

Sample	$^7Li/^6Li$[a]	^7Li[b]	Method[c]	References
Mechanisms				
High-energy galactic cosmic rays	1.60	−870	Spectra and model	Meneguzzi et al. 1971
Spallation	2.00	−830	Ion microprobe	Eugster and Bernas 1971
Astration (predicted bulk Sun)	10^6	$+8.3 \times 10^7$	Spectra and model	Delbourgo-Salvador et al. 1984
Extraterrestrial samples				
Sunspots	33	+1700	Spectra and model	Ritzenhoff et al. 1997
Solar wind in lunar soils	31 ± 4	+1600 ± 300	Ion microprobe	Chaussidon and Robert 1999
Lunar basalts	12.0603–12.0968	+3.35 to +6.39	MC-ICP-MS	Magna et al. 2006
Chondritic meteorites (average)	12.0200	0	MC-ICP-MS	McDonough et al. 2003
Orgueil (whole rock)	12.0669	+3.9	TIMS	James and Palmer 2000
Murchison (whole rock)	12.0654	+3.78 ± 0.21	MC-ICP-MS	Sephton et al. 2004
Murchison carbonate-rich acetic acid soluble phase	12.1708–12.1766	+12.55 ± 0.17 to +13.03 ± 0.25	MC-ICP-MS	Sephton et al. 2004
Murchison phyllosilicate-rich matrix	12.0901–12.0940	+5.83 ± 0.61 to +6.16 ± 0.78	MC-ICP-MS	Sephton et al. 2004
Murchison chondrule	11.9969	−1.92 ± 0.31	MC-ICP-MS	Sephton et al. 2004
Mokoia chondrules	11.3745–12.0182	−53.7 to −0.15	Ion microprobe	Robert and Chausidon 2003
Semarkona chondrules (average)	12.1402	+10	Ion microprobe	Chaussidon and Robert 1998
Vesta	12.0565–12.0891	+3.04 to +5.75	MC-ICP-MS	Magna et al. 2006
Terrestrial samples				
Silicate earth	12.0681	+4.0	Mass balance calculation	Teng et al. 2004
Mid-ocean ridge basalt	12.0609–12.0765	+3.4 ± 4.7	TIMS	Chan et al. 1992

[a]$^7Li/^6Li$ ratios are calculated using the δ equation and the absolute $^7Li/^6Li$ value for the L-SVEC standard (12.02).
[b]Number of significant figures reflects the precision of the analysis.
[c]TIMS = thermal ionization mass spectrometry; MC-ICP-MS = multi-collector inductively coupled plasma mass spectrometry.

following the method described in James and Palmer (2000). Lithium isotope ratios were measured using a Nu Instruments multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS). Each result represents an average of 20 measured ratios with the background measured before analysis subtracted. Individual analyses were bracketed by measurement of the L-SVEC standard (Flesch et al. 1973) that has a concentration within 10% of that of the sample. A 10 ppb solution and solution uptake rate of 80 μl min^{-1} produces a typical beam intensity of ~1 V compared with a background of 3 mV. The internal precision on $^7Li/^6Li$ measurements is usually <±0.15‰ (2σ) for a 10 ppb solution; this increases with decreasing lithium concentration and is typically <±0.65‰ (2σ) for a 2 ppb solution. The external precision of this technique, determined by 8 analyses of 5 separate preparations of seawater analyzed at the same time as the samples, is ±0.66‰ (2σ).

In this report the isotopic ratios of the samples are expressed as δ^7Li values (in ‰) relative to the L-SVEC standard as follows:

$$\delta^7Li = \left[\frac{(^7Li/^6Li)_{standard} - (^7Li/^6Li)_{standard}}{(^7Li/^6Li)_{standard}} \right] \times 1000$$

RESULTS AND DISCUSSION

Whole Rock Measurements

Table 1 contains the results of lithium isotopic analyses of whole rock Allende and its dark inclusions. These data can be compared to previously published data of extraterrestrial and terrestrial sources and materials (Table 2; updated from Sephton et al. 2004). Our measured value for whole rock Allende (+2.0‰) is within the range of literature values for carbonaceous chondrites, i.e., between −5‰ and +5‰ and in accord with previously published δ^7Li values for this meteorite (+1.7‰ ± 1 [McDonough et al. 2003] and +3.1‰ [Magna et al. 2006]). This δ^7Li value is relatively high for a type III meteorite and has been interpreted as the result of an early period of aqueous processing which was preserved when dehydration occurred during subsequent thermal metamorphism (McDonough et al. 2003).

Previously studied examples of aqueously altered chondritic material are provided by the Murchison (CM2) and Orgueil (CI1) meteorites (Table 2). Published δ^7Li values for Murchison and Orgueil are +3.8‰ (Sephton et al. 2004) and +3.9‰ (James and Palmer 2000) respectively reflecting an increased relative abundance of ^7Li-rich phyllosilicates and

carbonates in the lower petrographic type meteorites (Table 2).

It is logical to assume that if the Allende dark inclusions were initially produced by greater levels of aqueous processing relative to the whole rock, they will have lithium isotopic compositions similar to those of Murchison and Orgueil and therefore will be isotopically distinct from the whole rock meteorite. Subsequent thermal dehydration of the dark inclusion material will not have altered any enrichment in ^{7}Li brought about by the action of liquid water. Any later-stage, parent body–wide aqueous alteration is also unlikely to have homogenized any difference in lithium isotope ratios of dark inclusions and the whole rock. It is conceivable that the Allende dark inclusions themselves may be the cause for the relatively high whole rock δ^7Li value for a type III meteorite.

Bulk values for Allende dark inclusions range from +1.8‰ to +2.6‰, which is within error of the range determined for the whole rock meteorite. Thus, we conclude that there is no compelling evidence of past aqueous processing of the dark inclusions. Furthermore, these data imply that the dark inclusions are not the cause of the relatively high Allende whole rock δ^7Li value.

Acetic Acid Leachate Data

Leaching with acetic acid isolates any aqueously generated carbonate present along with other acetic acid soluble phases (which are likely to include Fe-oxides and Fe-oxyhydroxides) from acetic acid insoluble phases (which are mainly silicates and some refractory minerals). Acetic acid leaches have been performed previously for Murchison and revealed a significant enrichment in ^{7}Li in this fraction (+12.6‰ to +13.0‰) (Sephton et al. 2004).

The δ^7Li values for the whole rock Allende and dark inclusions acetic acid leachates are significantly different from the values obtained from Murchison. For Allende, the whole rock and acetic acid leachate data are within error and thus isotopically homogenous. In contrast, Murchison data suggest that aqueous processing imparts substantial ^{7}Li enrichments into acetic acid soluble phases. The homogeneity of the Allende data implies a relatively small amount of ^{7}Li-rich, aqueously generated carbonates in the whole rock meteorite and dark inclusions and therefore a relatively limited amount of parent body alteration.

Water Leachate Data

The amounts of lithium isolated from the water leachates (0.8–6.2 ppb) is commonly <0.5% of the lithium content of the bulk samples. It is extremely difficult to obtain precise δ^7Li measurements for such low levels of lithium. Furthermore, all of the water leachate values that we report in Table 1 are isotopically heavy but insignificant for the lithium

isotope balance of the bulk sample; for example, the δ^7Li value of the water leach would need to be >+42 ‰ to increase the δ^7Li of the bulk by >0.2 ‰.

CONCLUSIONS

Lithium isotope analysis by MC-ICP-MS indicates that Allende dark inclusions and the whole rock meteorite exhibit no resolvable difference in isotopic composition. Lithium isotopes are readily affected by aqueous processing, with ^{7}Li passing preferentially into solution. Consequently, mineral phases affected by aqueous fluids commonly exhibit an enrichment in ^{7}Li. The similarity in isotopic composition for dark inclusions and whole rock meteorite suggests that commonly proposed origins of Allende dark inclusions by a relatively elevated period of aqueous processing followed by thermal alteration and dehydration are an unlikely source of these unusual clasts. Overall, Allende may have experienced a complex alteration history, but based on lithium isotope data the aqueous and thermal record in the dark inclusions is not radically different from the rest of the meteorite.

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